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SYSTEMATIC BIASES IN MEASUREMENT OF URBAN NITROGEN DIOXIDE USING PASSIVE DIFFUSION SAMPLERS

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Abstract. Measurement of nitrogen dioxide using passive diffusion tube over 22 months in Cambridge, U.K. are analysed as a function of sampler exposure time, and compared with NO_2 concentrations obtained from a co-located chemiluminescence analyser. The average ratios of passive sampler to analyser NO_2 at a city centre site (mean NO_2 concentration 22 ppb) are 1.27 (n = 22), 1.16 (n = 34) and 1.11 (n = 7) for exposures of 1, 2 and 4-weeks, respectively. Modelling the generation of extra NO_2 arising from chemical reaction between co-diffusing NO and O_3 in the tube gave a ratio (modelled/measured) of 1.31 for 1-week exposures. Such overestimation is greatest when NO_2 constitutes, on average, about half of total NO_x (= NO + NO_2) at the monitoring locality. Although 4-week exposures gave concentrations which were not significantly different from analyser NO_2, there was no correlation between the datasets. At both the city-centre site and another semi-rural site (mean NO_2 concentration 11 ppb) the average of the aggregate of four consecutive 1-week sampler exposures or of two consecutive 2-week sampler exposures was systematically greater than for a single 4-week exposure. The results indicate two independent and opposing systematic biases in measurement of NO_2 by passive diffusion sampler: an exposure-time independent chemical overestimation with magnitude determined by local relative concentrations of NO and O_3 to NO_2, and an exposuretime dependent reduction in sampling efficiency. The impact of these and other potential sources of systematic bias on the application of passive diffusion tubes for assessing ambient concentrations of NO_2 in short (1-week) or long (4-week) exposures are discussed in detail.

Keywords: air monitoring, chemical model, nitrogen oxides, passive sampler

1. Introduction

The pivotal role of nitrogen dioxide (NO_2) in many chemical processes in the atmosphere (for example the production of tropospheric ozone, O_3) and the potential impact on human health, has led regulatory agencies around the word to establish various air quality standards for atmospheric concentrations of NO_2. In the U.K., limit values for NO_2 of 150 and 21 ppb (part in 10^9 by volume), measured as hourly and annual averages, respectively, have been introduced, based at this stage on protection to human health (DoE, 1997). These standards are in addition to the EC Directive 85/203 and require compliance by the end of 2005 irrespective of whether the location is kerbside, urban background, or rural.

The passive diffusion tube has been used for many years to measure outdoor concentrations of NO_2 across rural (e.g. Atkins and Lee, 1995) and urban (e.g. Campbell *et al*., 1994) national networks, and for more local scale concentration variations (e.g. Hewitt, 1991; Van Reeuwijk *et al.*, 1998; Kirby *et al*., 1998). The increased emphasis on NO_2 as an air pollutant, a result in part of the fact that concentrations of NO_2 in urban areas have not declined in recent years, and the current requirement for U.K. local authorities to review air quality in their areas, make it likely that passive samplers will increasingly be used for wide-area assessment of NO_2 compliance.

For these reasons, therefore, it is important that potential sources of error or limitations to passive sampler measurement are recognised. Various evaluation studies of NO_2 passive diffusion tubes (e.g. Atkins *et al*., 1986; Moscheandras *et al*., 1990; Hedley *et al*., 1994; Gair and Penkett, 1995; Shooter *et al.*, 1997, Heal and Cape,

1997) have identified a number of possible confounding processes; for example, lack of chemical specificity to NO_2, wind-induced shortening of diffusion path, or overestimation caused by chemical reaction between co-diffusing NO and O_3 in the tube to produce additional NO_2.

Evidence from a recent field trial with passive diffusion tubes and continuous analysers in the centre of Edinburgh, U.K. (Heal *et al*., 1999) has corroborated the suggestion of systematic chemical overestimation of NO_2 by within-tube chemistry between NO and O_3 also diffusing in from the ambient air.

In this paper, data from an entirely independent and much longer (22 months) study between passive diffusion samplers and continuous analysers from the city of Cambridge, U.K. are analysed and compared with numerical model predictions of the extent of chemical overestimation. The results substantiate a conclusion of systematic over-reading of passive diffusion samplers because of chemical interference. Moreover, a thorough investigation of three different sampler exposure times also suggests that passive diffusion tube measurement of NO_2 is subject to an additional exposure-time dependent loss process. These findings have important implications for the interpretation of passive diffusion tube data against air quality standards, and particularly when comparing sampler data obtained under different exposure conditions.

2. Experimental Methods

Standard acrylic Palmes-type passive diffusion tubes (Palmes *et al*., 1976) were exposed in the centre of the city of Cambridge, U.K., between February 1995 and December 1996. Passive samplers were co-located with a chemiluminescence analyser, which provided hourly values for NO and NO_x (= NO + NO_2), and a continuous O_3 analyser, both operated by Anglia Polytechnic University. Analysers were Thermo-Environmental Instruments Model 42 and Model 49, respectively, operated in accordance with established protocols (AEA, 1993). The site was 20 m from a main road and classified as 'urban intermediate.'

For an 11 month period, parallel passive diffusion tube exposures of 1, 2 and 4-week duration were undertaken at both the city site and a second site at Impington, a semi-rural background site on the outskirts of the city. No continuous analyser data were available at the latter. Passive samplers were always deployed in duplicate and 96% of sampler values reported here were the means of at least two measurements. The mean (and range) in the values of relative standard deviation for all replicate exposures indicated a high level of precision and were as follows: 1-week (n = 30), 3.1% (0.0–8.3%); 2-week (n = 41), 4.2% (0.3–10.5%); 4-week (n = 10), 4.6% (1.3–9.7%). Full details of the sampling protocol and an evaluation of factors affecting sampler performance, including precision, will be reported separately.

The combined chemistry and diffusion numerical model developed by Heal and Cape (1997) was used to calculate total cumulative NO_2 trapped by the adsorbent of a passive diffusion tube when chemical reaction between NO and O_3 in the gas-phase diffusion regime between tube entrance and adsorbent was included. In the model the one-dimensional continuity equation for diffusion and reaction of each of NO_2, NO andO_3 is solved numerically by finite differences. The boundary conditions at the open end of the tube are the appropriate data-set of hourly concentrations of NO, NO_2 and O_3 recorded by the co-located continuous analysers. The boundary condition for NO_2 at the adsorbent is modelled as an infinite sink, as is the case for a real sampler. There is no modelled loss of NO or O_3 at the adsorbent. The extra NO_2 calculated as arising from gas-phase reaction in the tube is fairly

insensitive to assumptions about the extent of penetration through the acrylic tube walls of UV light appropriate to NO_2 photolysis, because the value of $J(NO_2)$ (the photolysis coefficient for photolysis of NO_2 to NO and O) is usually sufficiently small that the timescale of photolysis is long compared with the average diffusion time in the sampler tube (Heal *et al*., 1999).

3. Results

3.1. Evidence for chemical over-estimation by passive diffusion tubes

Model simulations were performed for all passive sampler exposures at the city centre site for which complete sets of hourly analyser data were available. Time series of passive sampler measurements, model calculated NO_2 and exposure-average analyser NO_2 are shown in Figures 1a–c for all available data for 1, 2 and 4-week exposures. Comparisons over 2-week exposures are available for a 22 month time series. A statistical summary of the ratios and correlations between passive sampler, continuous analyser and model-simulated NO_2 values for all available

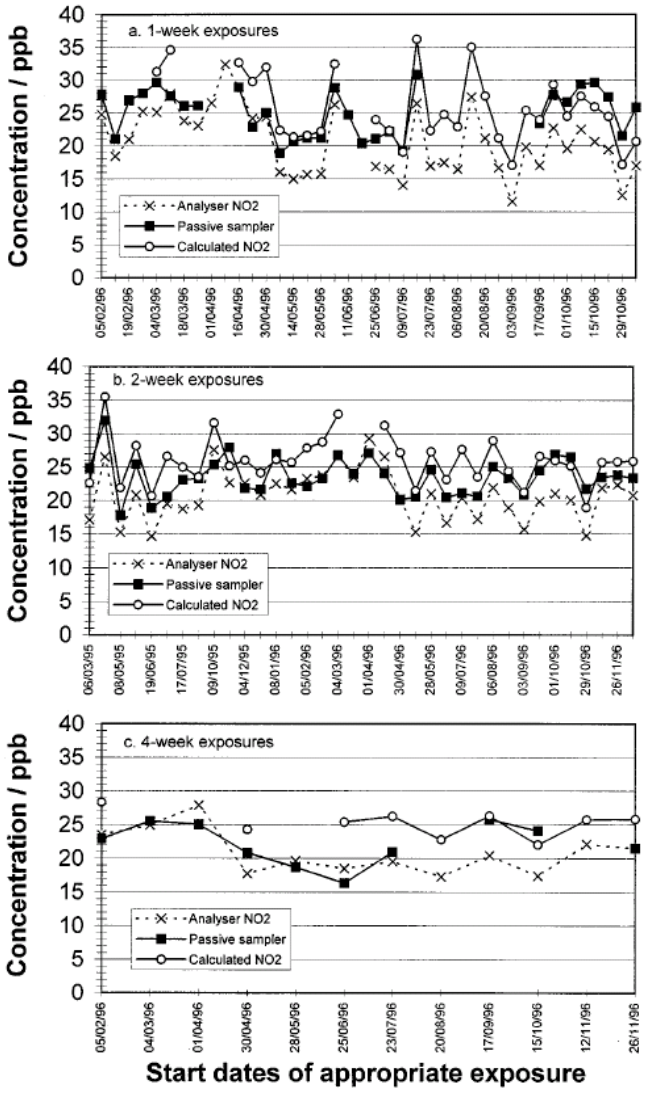

Figure 1. Time series plots of exposure-averaged passive sampler NO_2, analyser NO_2 and

model-simulated sampler NO_2 for a) 1-week, b) 2-week, and c) 4-week exposures at the Cambridge city centre site.

	Calculated NO_2/ analyser NO_2	Sampler NO_2/ analyser NO_2	Sampler NO_2/ calculated NO_2
1-week exposure			
No. of data pairs	22 (60)	22 (28)	22
Mean, range	**1.31**, 1.13–1.42 (**1.28**, 1.09–1.48)	**1.27**, 0.95–1.72 (**1.24**, 0.95–1.72)	**0.97**, 0.77–1.25
Corr. coeff.		0.79*** (0.80***)	0.74***
Paired difference		Sig.***	Not Sig.
2–week exposure			
No. of data pairs	34	34 (36)	34
Mean, range	**1.27**, 1.11–1.43	**1.16**, 0.91–1.47 (**1.15**, 0.91–1.47)	**0.91**, 0.74–1.15
Corr. coeff.		0.66*** (0.67***)	0.63***
Paired difference		Sig.***	Sig.***
4–week exposure			
No. of data pairs	7 (9)	7 (10)	7
Mean, range	**1.29**, 1.20–1.37 (**1.28**, 1.16–1.37)	**1.11**, 0.88–1.39 (**1.06**, 0.88–1.39)	**0.86**, 0.64–1.09
Corr. coeff.		0.25 (0.54)	–0.02
Paired difference		Not Sig.	Sig.*

TABLE I
Summary data for average concentration of NO_2 (in ppb) from continuous analyser, passive diffusion sampler, and model simulated passive sampler, for exposure periods of 1, 2 and 4-weeks for those exposures where all three of these measures are available. (Values in parentheses refer to all data available for the data pair calculated NO_2, analyser NO_2 and for the data pair sampler NO_2, analyser NO_2). The significance level is indicated as follows: Not.Sig. = $P > 0.05$; * = $0.01 < P < 0.05$; ** = $0.001 < P < 0.01$; *** = $P < 0.001$

data at each exposure time, and for the subset of data where all three measures are available, is given in Table I (paired data compared using *t*-tests).
In all instances exposure-averaged NO_2 concentrations calculated from model

simulations exceed the corresponding average analyser NO_2 for that period. This is an inevitable consequence of the co-existence of NO and O_3 at the entrance to the tube. The calculated overestimation ranges from 11 to 48% for all available data (average 28%) and demonstrates the extent of potential systematic error in measurement of NO_2 arising from chemical reaction in the sampler.

The general trend in Figure 1 and Table I is that NO_2 concentrations from 1-week exposed passive samplers exceed actual analyser NO_2 by the most, whilst NO_2 concentrations from 4-week exposed samplers are closest to analyser NO_2 and 2-week exposed sampler concentrations are intermediate. There is no evidence from Figure 1 of any seasonal trends.

For 1-week exposures, average sampler to analyser over-reading is 27% which compares well with the average model-simulated over-reading of 31% for the same 22 1-week exposures (Table I). Scatter plots of model-simulated NO_2 and sampler NO_2 for each exposure time are shown in Figures 2a–c. The significant correlation coefficient for the 1-week exposures (Figure 2a) shows that agreement between observed and calculated over-reading is systematic and does not occur by chance.

Average over-reading of passive samplers relative to analyser NO_2 over 34 2-week exposure periods was 16%, compared with the average model calculated over-reading of 27%. Although correlation between measured and simulated NO_2 is significant there is significant difference between the magnitude of the values.

In 7 4-week exposures passive samplers over-read analyser NO_2 by an average of 11% compared with an average calculated over-reading of 29%. There is no relationship between measured and model-simulated NO_2, although inevitably the data set is smaller.

3.2. Evidence for exposure-time dependent loss of NO_2 in passive diffusion tubes

Concurrent 1, 2 and 4-week passive sampler exposures were undertaken at the Cambridge city centre and Impington semi-rural sites exposures between February and December 1996.

The effect of exposure duration on sampler performance was investigated by comparing the NO_2 derived from 4-week exposures with the average concentrations derived from i) summing the cumulative NO_2 measured in the two consecutive 2-week exposures of that four week period (denoted 2*2-week), and ii) summing the cumulative NO_2 measured in the four consecutive 1-week exposures of that four week period (denoted 4*1-week).

The ten sets of data from the city centre site (7 complete sets) are shown in Figure 3a. Without exception, NO_2 concentrations derived from 4*1-week exposures are greater than concentrations derived from both 2*2-week exposures ($P < 0.001$) and 4-week exposures ($P < 0.01$). The NO_2 concentrations from the 2_2-week exposures are significantly greater ($P < 0.05$) than the corresponding 4-week exposures. All correlations between 4-week, 2*2-week and 4*1-week values are significant indicating that measurements vary in the same way regardless of differences in magnitude.

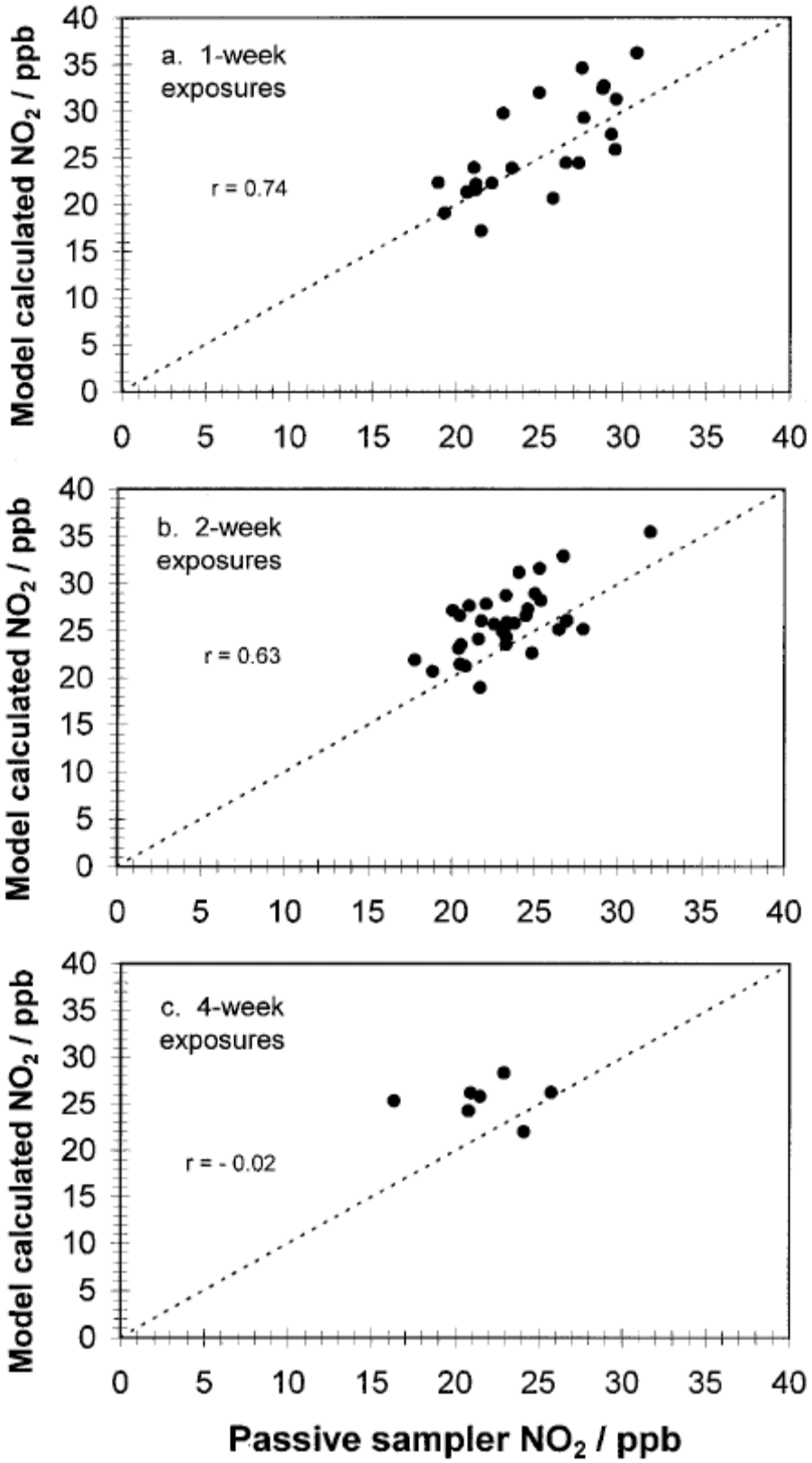

Figure 2. Relationship between model-simulated sampler NO2 and passive sampler NO2 fora) 1-week, b) 2-week, and c) 4-week exposures at the Cambridge city centre site.

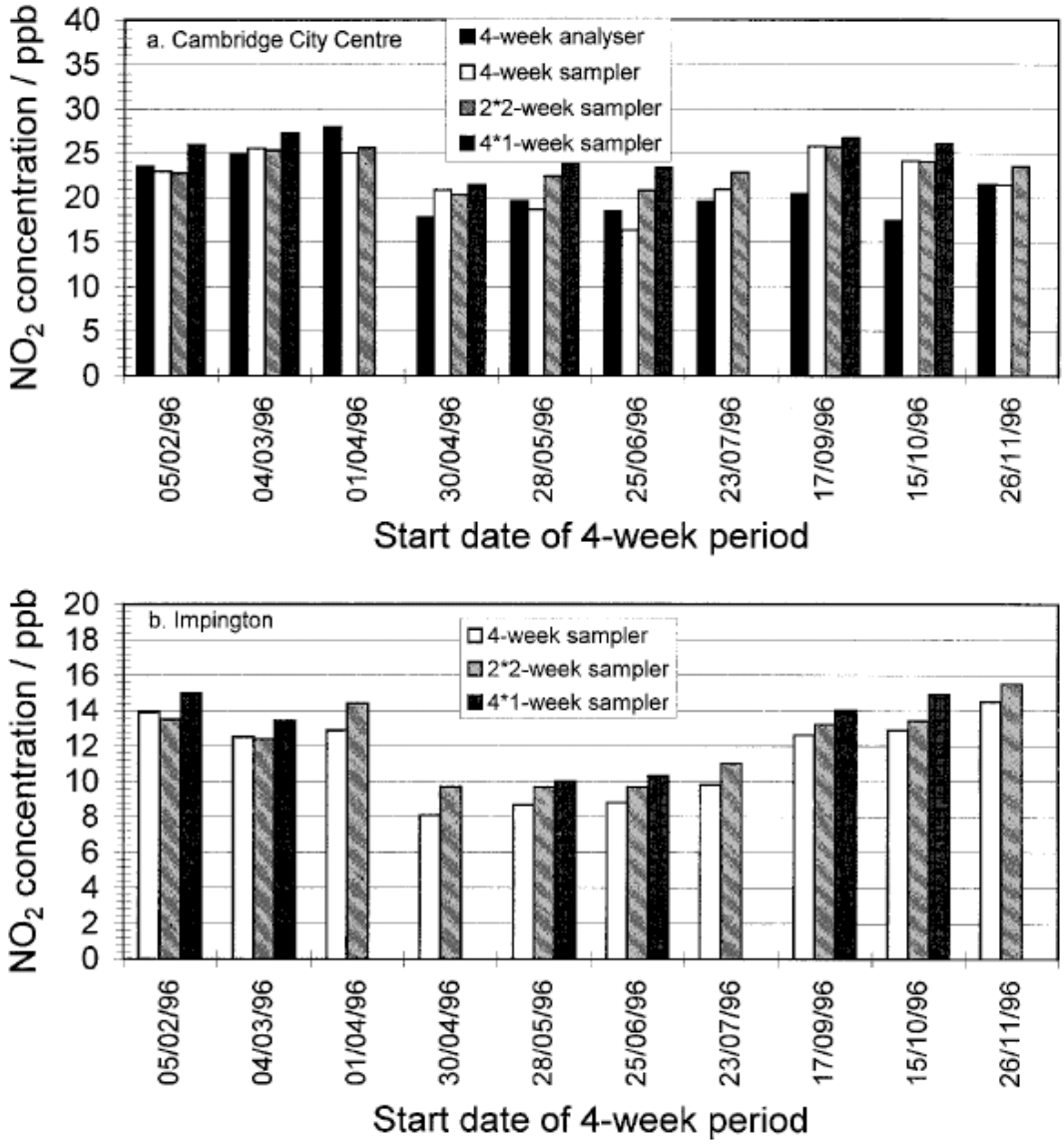

Figure 3. A comparison between 4-week sampler NO_2, the average of two 2-week sampler NO_2, and the average of four 1-week sampler NO_2 at a) Cambridge city centre site, b) Impington semi-rural site. (Analyser data available only at the city centre site). Note the different scales.

As has been noted in Section 3.1, concentrations of NO_2 derived from 4-week passive sampler exposures are not significantly different from 4-week exposure averages of analyser NO_2 whereas both 4*1-week and 2*2-week derived concentrations of NO_2 are significantly greater than that from the continuous analyser ($P < 0.001$ and $P < 0.05$, respectively).

Analogous data from the semi-rural site are shown in Figure 3b. The same systematic trends are apparent; concentrations derived from combining short-term exposures (4*1-week) are significantly greater than concentrations derived from 2*2-week exposures ($P < 0.01$) which, in turn, are significantly greater than 4-week concentrations ($P < 0.01$).

4. Discussion

The average ratios between sampler and analyser NO_2 (for all available data) decrease in the order 1.24, 1.15, 1.06 for exposure lengths of 1, 2 and 4-week respectively (Table I). At the same time the average ratio between passive sampler and model simulated NO_2 decreases in the order 0.97, 0.91, 0.86, with a corresponding decrease in the significance of the relationship between sampler and model simulated values. The model simulates well the extent of chemical overestimation for 1-week exposures, but accuracy (closeness to unity in ratio of sampler to model simulated NO_2) and precision (significance of correlation) decrease for longer exposures of 2 and 4-weeks. The *in-situ* comparisons of three different exposure times (Section 3.2) highlight a trend for cumulative absorbed NO_2 in passive samplers to decrease with exposure time.

The observations are consistent with the existence of two opposing systematic errors:

- an overestimation of NO_2 by chemical reaction that depends on relative concentrations of NO,NO_2 and O_3 in the sampling locality, but not on accumulated NO_2,

- a net reduction in NO_2 sampling efficiency, related in some way to length of exposure period (i.e. to accumulated NO_2) such as a loss process or other limiting mechanism at the adsorbent.

The two processes are independent of each other. The apparent greater accuracy of 4-week exposures relative to the continuous analyser arises because of cancellation (on average) of the two effects rather than an intrinsic relation between them. The increasing contribution of the loss process produces the greater variation in the distribution of NO_2 values from 4-week exposures compared with 1-week exposures.
There is no apparent seasonal trend to the loss process.
A simple model can be constructed to describe the combined effects of the two biases and to extract an estimate of the magnitude of the loss process. The expression linking cumulative NO_2 sampled, Q, in time t, to the average concentration of NO_2 in the air during the exposure, C, is,

$$Q = \frac{C A D t}{L} \qquad (1)$$

where D (0.154 $cm^2 s^{-1}$, Palmes *et al*. (1976)) is the diffusion coefficient of NO_2 in air, and A (0.96 cm^2) and L (7.1 cm) the internal cross-section and length of the sampler, respectively. The sampling rate (Q/t) depends only on physical parameters, and has magnitude 75 C ppb $cm^3 h^{-1}$ when appropriate parameters are substituted for ambient concentration, C, in ppb. This sampling rate in the absence of any bias can be denoted by Γ_{diff}. The contribution of chemical reaction in the tube can be treated as equivalent to an extra sampling rate, Γ_{chem}. In this study, average chemical overestimation was about 28% (Section 3.1) so $\Gamma_{chem} \sim 21$ C ppb $cm^3 h^{-1}$. If the loss process is represented as a first-order loss coefficient, k_{loss}, acting on cumulative NO_2, then the equation for rate of accumulation of NO_2 at the adsorbent is given by,

$$\frac{d\,NO_2}{dt} = \Gamma_{diff} + \Gamma_{chem} - k_{loss}\,NO_2 \quad (2)$$

The accumulated NO_2 in time, t, obtained by integration of Equation (2), is given by,

$$(NO_2)_t = \frac{(\Gamma_{diff} + \Gamma_{chem})}{k_{loss}}(1 - e^{-k_{loss}\,t}) \quad (3)$$

from which the corresponding exposure-averaged NO_2 is readily derived if required. The situation described by Equation (3) corresponds to observed 'sampler NO_2.' Likewise, the situation when only the standard sampling rate is considered, $(NO_2)t = 0_{diff}\,t$ corresponds to 'analyser NO_2' (i.e. true NO_2), while the situation where sampling rate includes extra chemical generation, but not loss, i.e. $(NO_2)t = (\Gamma_{diff} + \Gamma_{chem})\,t$, corresponds to 'calculated NO_2'.

Figure 4 shows a plot of cumulative NO_2 over a 4-week exposure period (for an illustrative constant ambient NO_2 concentration of 20 ppb) using the expressions $\Gamma_{diff}\,t$, $(\Gamma_{diff} + \Gamma_{chem})\,t$ and Equation (3), with a value of k_{loss} chosen for the latter expression to satisfy as closely as possible the various observed average ratios between sampler, calculated and analyser measurements after 1, 2 and 4-week exposures (Table I). The value of k_{loss} which best describes the observed data is around $5.0*10^{-4}\,h^{-1}$ i.e. a lifetime with respect to loss of accumulated NO_2 in the tube of ~83 days. For comparison with experimental ratios in Table I, the ratios of 'sampler' to 'analyser' after 1, 2 and 4-weeks for this k_{loss} fit shown in Figure 4 are 1.23, 1.17 and 1.09, respectively, and the ratios of 'sampler' to 'calculated' are 0.96, 0.92 and 0.86, respectively.

What is the origin of the loss process? It is interesting to note that the same phenomenon was apparent at the semi-rural site (where the long-term average of 4-week NO_2 concentrations over 11 months was only ~11 ppb) as at the citycentre site (where the equivalent long-term average concentration was ~22 ppb).

A small trial comparing normal acrylic tubes with quartz glass (UV-transmitting) and foil-covered (opaque) tubes has suggested that the magnitude of this exposuretime dependent loss may be related to the potential for photolytic flux into the tube (Heal *et al.*, 1999). Although photolysis does not affect gas-phase NO_2 diffusing along the tube, even a small flux of UV reaching the adsorbent either by a

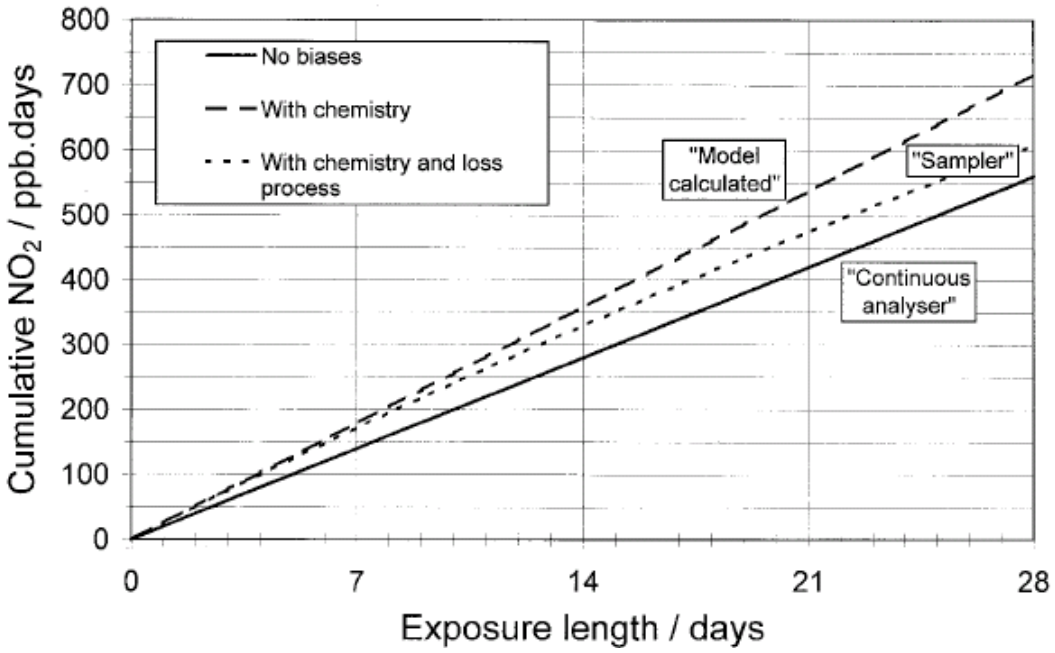

Figure 4. Simulations of cumulative NO_2 in a passive sampler over a 4-week exposure for different combinations of systematic bias. See main text for explanation.

small transmission through the walls, or by internal reflections from the entrance, would be sufficient to cause an exposure-dependent loss on the timescale of days and weeks, through degradation of bound nitrite at the triethanolamine (TEA) absorbent. The magnitude of k_{loss} estimated above ($\sim 1.4 * 10^{-7}$ s^{-1}) is some 4 orders of magnitude smaller than average ambient photolysis coefficient, $J(NO_2)$, for gas-phase NO_2.

Alternative possible explanations for exposure-dependent loss include biological degradation of adsorbed nitrite, or limitations to adsorbent capacity caused by, for example, insufficient diffusion of NO_2 into the bulk of the TEA absorbent. If it is assumed that NO_2 does not desorb once it has complexed with TEA, then uptake rate at the absorbent will not be affected by exposure time, provided that diffusion is sufficiently fast, and the total number of TEA molecules exceeds cumulative NO_2 required. In this study, sampler grids were prepared using 30µ of 10% v/v solution of TEA in water ($\sim 2 * 10^{-5}$ moles TEA) which is about a factor 10^2–10^3 larger than NO_2 sampling capacity required for a 4-week exposure. However, this TEA-NO_2 capacity corresponds to coverage to at least 10^2 molecular layers of absorbent on the grid, so molecular diffusion within the absorbent is required to expose fresh TEA at the surface or to permit reaction of NO_2 with 'bulk' TEA. An absorbent diffusion coefficient of 10^{-9} cm^2 s^{-1} suggests that diffusion is sufficient, but nevertheless time-dependent limitations arising from a combination of some of these (or other) factors cannot be ruled out on the basis of existing data.

The average model calculated overestimation for 1-week exposures was 31% whereas average observed overestimation for the same periods was 27%. Whilst agreement is good, a number of other factors could contribute to systematic biases: i) action of the loss process over 1-week (but this is small, see Figure 4); ii) exclusion in the numerical model of UV flux into the tube that would photolyse gas-phase NO_2 during diffusion; iii) systematic errors in continuous analyser data, or in parameters used to derive exposure-average NO_2 from cumulative NO_2 in the passive samplers.

The loss process has been discussed above. Previous work has shown that acrylic tubes transmit less than 20% of $J(NO_2)$ (Heal and Cape, 1997). Furthermore, since $J(NO_2)$ varies diurnally (to zero at night) and with season, the effect of photolysis on NO_2 in the tube within the diffusion time-scale is further reduced. Heal *et al*. (1999) have shown that inclusion of 20% transmission of $J(NO_2)$ appropriate to the exact time in the exposure has negligible impact on cumulative NO_2 reaching the adsorbent for sampler exposures during winter and only a few % reduction in calculated overestimation during summer exposures. This is because the timescale for $NO + O_3$ reaction is comparable with diffusion residence time along the tube (2–3 min on average), whereas the photolytic lifetime of NO_2 at small $J(NO_2)$ is considerably longer.

It is appropriate also to discuss other possible systematic errors. It is assumed throughout that chemiluminescence analyser NO_2 represents true NO_2 in the air (and likewise for the O_3 analyser). Operation and calibration of continuous analysers in this study were in accordance with accepted protocols (AUN, 1993). Variation within quoted analyser precision ($<$0.2 ppb) and baseline drift ($<$0.5 ppb d^{-1}) has only a small effect on concentration of NO_2 measured in urban areas. However, NO_2 concentration is obtained indirectly *via* thermal reduction to NO, so the output value of analyser NO_2 includes a small contribution from peroxyacetylnitrate (PAN) and nitrous acid (HONO). In the U.K. the contribution is small (a few % of total NO_2) but the error is systematic and in a direction so as to increase further the observed over-reading of passive sampler relative to analyser values. This potential source of bias may be offset, however, since it is likely that both HONO and PAN are also trapped by TEA and detected as nitrite.

The major uncertainty in deriving NO_2 concentrations from passive samplers is the dependence of the sampling rate on the diffusion coefficient of NO_2 in air. The value of 0.154 $cm^2\ s^{-1}$ from Palmes *et al*. (1976) is for a temperature of 294 K, rather higher than average ambient temperature in the U.K. The recent comprehensive review of molecular diffusivities by Massman (1998) recommends the temperature dependent expression $D(T) = 0.1361(T/273)^{1.81}$ for NO_2 in air, in close agreement at 294 K with the Palmes *et al*. (1976) value. The key point, however, is the fairly strong temperature dependence of the diffusion coefficient. Use of an uncorrected value of D in Equation (1) when average temperature during passive sampler exposure is actually 283 K results in a systematic underestimation of 7% in exposure-averaged NO_2 concentration (expressed in units of mass per

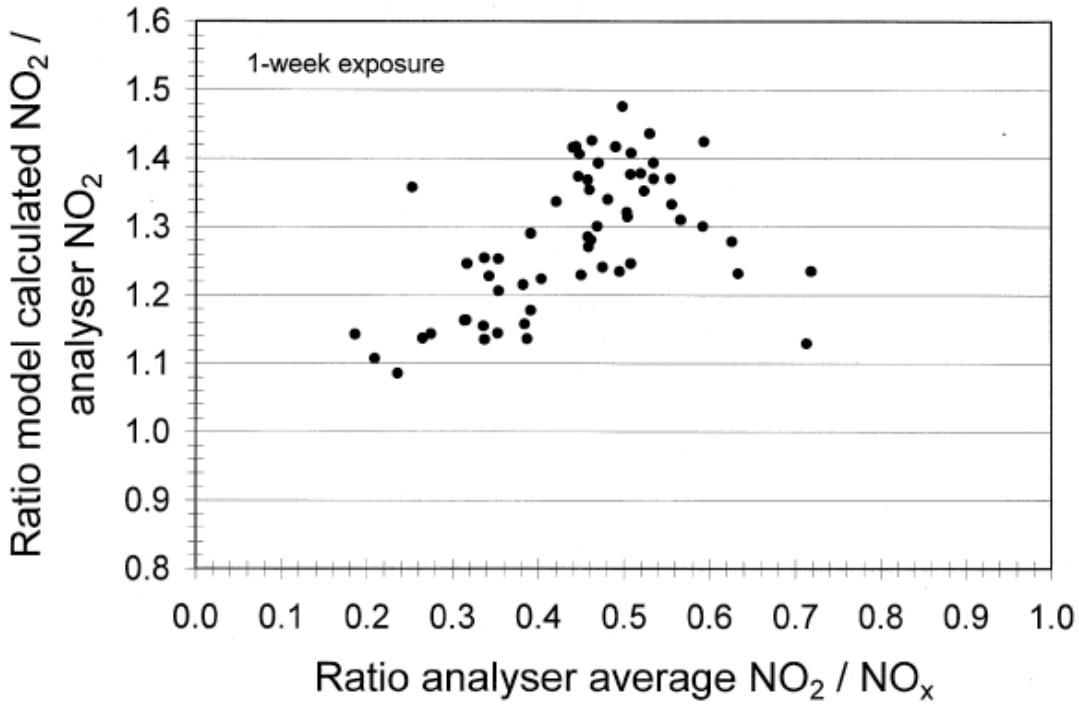

Figure 5. The relationship between extent of model simulated overestimation of sampler NO_2 and the ratio of weekly average NO_2 to NO_x during the exposure period.

volume) calculated from accumulated NO_2^-. The temperature dependence reduces to $T^{0.81}$ when sampler-derived NO_2 is calculated as a mixing ratio (ppb) rather than a concentration, but neglecting even this temperature dependence still leads to a 3% underestimation in NO_2 concentration from passive samplers for a 10 K temperature change. Such discrepancies are generally within the precision of diffusion samplers but it is important to note that again these are systematic and not random errors.

The magnitude of the chemical bias depends on the relative concentrations of NO and O_3 to NO_2 during exposure. In this study, in an urban area 20 m from a main road (a strong primary source of NO), extra NO_2 generated by chemical reaction in the sample tube was on average about 28% more than actual NO_2, for air in which the fraction of NO_2 to NO_x was, on average, about 0.5. However, there is a non-linear relationship between calculated chemical overestimation for 1-week exposures (using hourly input data) and the fraction of 1-week average analyser NO_2 to NO_x, as shown in Figure 5. The relative importance of chemical overestimation rises to a maximum as the proportion of NO (which may be converted to NO_2) to NO_2 increases, but declines again when NO is in large excess of NO_2 since under these conditions ambient air outside the sampler is likely to be strongly depleted in O_3 (because of rapid NO + O_3 reaction) and concentration of O_3 becomes the limiting factor for generation of extra NO_2 in the tube.

Although the exact extent of overestimation depends on the way in which concentrations of NO_2, NOand O_3 all fluctuate with respect to each other on relatively short timescales throughout the exposure, the usefulness of Figure 5 is that it permits crude estimation of the magnitude of chemical bias given the general relationship between average NO_2 and NO_x at a particular locality. It turns out that for this urban site in Cambridge, the average concentrations of air pollutants were such as to be in the regime that maximises the significance of chemical overestimation

in the curve of Figure 5. This is likely to be a fairly general scenario, applicable to many city centre or kerbside measurement locations.

A final consideration in discussion of systematic bias is the possibility of a shortening of the diffusion path in the tube caused by air movement across the exposed entrance. Such a process would also lead passive samplers to over-read NO_2 and would be independent of chemical overestimation except that chemical overestimation would be very slightly reduced because of shorter average residence time (and therefore NO to NO_2 reaction time) in the tube. However, the ability of the model simulations to account well for observed sampler NO_2 concentrations, in this study and the one in Edinburgh (Heal *et al*., 1999), suggest that wind-induced sampling error was not significant in these exposures. This does not preclude the possibility of other situations where wind might cause air motions within the tube and bias the results.

5. Conclusions for Application of Passive Samplers to Measurement of NO_2

Analysis of sampler data unequivocally indicates two opposing sources of bias in measurement of NO_2 by passive diffusion tube. First, samplers intrinsically overestimate NO_2 because of reaction in the tube between co-diffusing NO and O_3.

Secondly, cumulative NO_2 sampled by passive samplers decreases proportionately as exposure time increases.

The significance of the first source of bias depends on the relative concentration of NO and O_3 to NO_2 during the exposure, and is not dependent on exposure time other than through the way in which the trace gas concentrations vary. In the majority of urban monitoring localities, within short distances of traffic emissions, local NO, NO_2 and O_3 conditions are likely to be comparable to those shown to cause significant chemical overestimation of 10–50%. In semi-rural and rural applications, however, where NO concentrations are small compared with NO_2, this source of error will be insignificant.

The second source of error is likely to exist whatever the sampling location, even if the diffusion tube is considerably shaded, although the impact may vary slightly with season. There is a possibility, therefore, that 4-week exposures in rural areas may actually underestimate true NO_2 concentration because long-term losses are not offset by extra NO_2 generated in the tube. An underestimate by 4-week exposure passive samplers may also occur at very highly NO_x polluted sites, at which O_3 is consistently depleted to negligible concentrations relative to NO_2, so that resultant % chemical overestimation is again small compared with long-term loss. Preliminary data from a kerbside site in central London, at which average analyser NO_2 is about 50 ppb, support this conclusion.

A conclusion from this study, and the separate study in Edinburgh (Heal *et al*., 1999), is that 4-week exposures provide a worse measure of fluctuations in NO_2 concentration at a given location than 1-week exposures, (although it is possible that the significance evidence for this conclusion is to some degree an artefact of the necessarily smaller data-set for long *versus* short exposures). Given the indeterminate reduction of NO_2 with longer exposures, regardless of the extent of chemical overestimation, it is recommended that 1-week exposures be used where possible and the value of NO_2 concentration obtained accepted as lying somewhere between true NO_2 and NO_x concentrations. The inference is therefore that if values from 1-week sampler exposures do not indicate an air quality failure, then limits for NO_2 as a specific target species are being achieved. Conversely, apparent exceedances of air quality criteria for NO_2 cannot be simply derived from passive sampler data.

Finally, given the evidence of time-dependent loss it is concluded that the procedure

of directly comparing data from the aggregation of four 1-week sampler exposures with that of 4-week exposures (DETR, 1998) be treated with caution.

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References

AEA: 1993, EUN site operators' manual, AEA Technology, NETCEN.

Atkins, D. H. F., Sandalls, J., Law, D. V., Hough, A. M. and Stevenson, K.: 1986, The measurement of nitrogen dioxide in the outdoor environment using passive diffusion tube samplers. United Kingdom Atomic Energy Authority, Harwell, Report AERE R 12133.

Atkins, D. H. F. and Lee, D. S.: 1995, Spatial and temporal variation of rural nitrogen dioxide concentrations across the United Kingdom. *Atmospheric Environment* **29**, 223–239.

Campbell, G. W., Stedman, J. R. and Stevenson, K.: 1994, A survey of nitrogen dioxide concentrations in the United Kingdom using diffusion tubes, July–December 1991. *Atmospheric Environment* **28**, 477–486.

DoE: 1997, The United Kingdom National Air Quality Strategy, No. 3043, HMSO, London.

DETR: 1998, U.K. nitrogen dioxide survey 1996. *AEAT-2779*. Department of the Environment, Transport and Regions, London.

Gair, A. J. and Penkett, S. A.: 1995, The effects of wind speed and turbulence on the performance of diffusion tube samplers. *Atmospheric Environment* **29**, 2529–2533.

Heal, M. R. and Cape, J. N.: 1997, A numerical evaluation of chemical interferences in the measurement of ambient nitrogen dioxide by passive diffusion samplers. *Atmospheric, Environment* **31**, 1911–1923.

Heal, M. R., O'Donoghue, M. A. and Cape, J. N.: 1999, Overestimation of urban nitrogen dioxide by passive diffusion tubes: a comparative exposure and model study. *Atmospheric Environment* **33**, 513–524.

Hedley, K. J., Shepson, P. B., Barrie, L. A., Bottenheim, J. W., Mactavish, D. C., Anlauf, K. G. and Mackay, G. I.: 1994. An evaluation of integrating techniques for measuring atmospheric nitrogen dioxide. *Int. J. Environ. Anal. Chem*. **54**, 167–181.

Hewitt, C. N.: 1991, Spatial variations in nitrogen dioxide concentrations in an urban area. *Atmospheric Environment* **25**, 429–34.

Kirby, C., Greig, A. and Drye, T.: 1998, Temporal and spatial variations in nitrogen dioxide concentrations across an urban landscape: Cambridge, U.K. *Environmental Monitoring and Assessment* **52**, 65–82.

Massman, W. J.: 1998, A review of the molecular diffusivities of H_2O, CO_2, CH_4, CO, O_3, SO_2, NH_3, N_2O, NO and NO_2 in air, O_2 and N_2 near STP. *Atmospheric Environment* **32**, 1111–1127.

Moschandreas, D. J., Relwani, S. M., Taylor, K. C. and Mulik, J. D.: 1990, A laboratory evaluation of a nitrogen dioxide personal sampling device. *Atmospheric Environment* **24A**, 2807–2811.

Palmes, E. D., Gunnison, A. F., DiMattio, J. and Tomczyk, C.: 1976, Personal sampler for nitrogen dioxide. *Am. Ind. Hyg. Assoc. J*. **37**, 570–577.

Shooter, D., Brimblecombe, P., Shooter, J., Lowe, D., Day, P. J. and Du, S.: 1997, Some characteristics and applications of nitrogen dioxide passive samplers. *Environmental Technology* **18**, 243–254.

Van Reeuwijk, H., Fischer, P. H., Harssema, H., Briggs, D. J., Smallbone, K. and Lebret, E.: 1998, Field comparison of two NO_2 passive samplers to assess spatial variation. *Environmental Monitoring and Assessment* **50**, 37–51.